SYNTHESIS AND CHARACTERIZATION OF POLYMER MODEL COMPOUNDS

FINAL REPORT

By

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INTRODUCTION AND DISCUSSION

Part A - SYNTHESIS PROCEDURES

The theme and objective of this contract was to provide a series of model polymer substances embodying known, specific concentrations of the types of oxygen functional groups known or postulated to be present in coals.

The materials chosen were a series of chemically modified polystyrenes, synthesized from commercial precursors using the generalized routes summarized in Figures 1 through 4.

The starting materials incorporated or were converted into species containing one functional group per aromatic ring; the reaction conditions for the chemical modification procedures were selected so as to effect specific change at that functional group, or a migration to a specific site on the same ring as that bearing the converting functional group, without changing the remainder of the polymer skeleton.

The modifications introduced to the structures thus provided polymers with the following pendant functional groups or combinations of functional groups:

(i) phenolic methyl ether (sample KP-A)
(ii)phenolic hydroxy (sample KP-1
(iii) aromatic aldehyde (sample KP-4)
(iv) aromatic carboxylic acid (sample KP-5)
(v) phenolic acetate (sample KP-6)
(vi) aromatic carboxylate, sodium salt (sample KP-21)
(vii) aliphatic ketone (sample KP-7)
(viii) aliphatic ketone + phenolic methyl ether (sample KP-8)
(ix) aliphatic ketoxime (sample KP-26)
(x) phenolic hydroxy + aliphatic ketone (sample KP-29)
(xi) aromatic ketone (KP-31)
(xi) alcoholic acetate (samples LL-1, KP-28)
(xii) benzylic ether (sample KP-27)
(xiii) 1,3-diketone (sample KP-11)

Other, commercially purchased polymers provided examples of
(xiv) benzylic chloride (from poly(vinylbenzyl chloride)
(xv) aliphatic carboxylic acid (from (poly(acrylic acid))
(xvi) aliphatic ketone (from (poly(vinyl methyl ketone))
(xvii) alcoholic hydroxy (from allyl alcohol/styrene copolymers)

The following figures summarize the conversion reactions. In the structures, R is taken to represent the residual polystyrene monomer unit lacking the indicated functional group(s), and R' the residual framework in an allyl alcohol/styrene copolymer.
Full details of the experimental procedures are given in Appendix 1 of the Report.
Samples of these synthesized and purchased polymers were transmitted to the Coal Research Laboratories, Edmonton, for examination by Raman, FTIR, and solid-state 13-C nuclear magnetic resonance spectroscopy.

Figure 1
Modifications from poly(p-Methoxystyrene)

$R.OCH_3$	$\xrightarrow{(AlCl_3)}$	R.OH
KP-A		KP-1
R.OH	$\xrightarrow{(Ac_2O)}$	$R.O.CO.CH_3$
KP-1		KP-6
R.OAc	$\xrightarrow{(AlCl_3)}$	$R.(OH, COCH_3)$
KP-6		KP-29
$R.OCH_3$	$\xrightarrow{(Ac_2O)}$	mixture of $R.O.CO.CH_3$ + $R.(OCH_3, COCH_3)$
KP-A		KP-8

Figure 2

Modifications from poly(Vinylbenzyl chloride)

$R.CH_2Cl$ ——(hydrolysis)——> $(R.CH_2)_2O$
KP-27

$R.CH_2Cl$ ——(oxidative hydrolysis)——> $R.CH{:}O$
KP-4

$R.CH_2Cl$ ——(OAc^- substitution)——> $R.CH_2.O.CO.CH_3$
KP-28

$R.CH{:}O$ ——(oxidation, MnO_4^-)——> $R.CO.OH$
KP-4 KP-5

$R.CO.OH$ ——(neutralization, NaOH)——> $R.CO_2^-$
KP-5 KP-21

Figure 3

Introduction of Carbonyl Functions into Polystyrenes

$R.H \xrightarrow{(Ac.Cl/AlCl_3)} R.CO.CH._3$ KP-7

$R.CO.CH_3$ KP-7 $\xrightarrow{(NH_2OH/pyridine)} R.C(:N.OH)CH_3$ KP-26

$RH \xrightarrow{(C_6H_5.COCl/AlCl_3)} R.CO.C_6H_5$ KP-31

$R.CO.CH_3$ KP-7 $\xrightarrow{(CH_3.CO.C_2H_5/NaH/THF)} R.CO.CH_2.CO.CH_3$ KP-11

Figure 4

Modification of Allyl alcohol/styrene copolymers

$R'.OH \xrightarrow{(Ac_2O/pyridine)} R.O.CO.CH_3$ LL-1

PART B - SPECTROSCOPIC CHARACTERIZATIONS

The polymer species offer similar difficulties to those of coal samples since their insolubility in common solvents precludes the use of many analytical techniques. Samples are not readily prepared for transmittance infrared methods using mulling or disk techniques, since the coherent polymers resist dispersion to fine particle sizes.
The difficulties of sample preparation are absent from photoacoustic spectra, and these were judged to be suitable as indicators of the quality and specificity of the conversions of the polymers, and in their general characterization. In addition, the frequencies diagnostic of functional groups in the solid phases offer comparable references to those likely to be observed for analogously derivatized coals (the diagnostic frequencies assembled in compendia such as Bellamy's The Infrared Spectra of Complex Molecules refer to solution spectra).

Therefore we have recorded the PAIFT spectra of all of our series of polymer samples using the Bruker IFS110 Spectrometer interfaced to the Princeton Applied Research 6003/6005 Photoacoustic Accessory System. Spectra were acquired using data points at 4 cm.-1 intervals, an instrumental interferometer mirror velocity setting of 2 (corresponding to 0.08333 $cm.s^{-1}$) and 128 or 256 co-added interferograms. The photoacoustic energy responses of the samples from 4,000 to 600 $cm.^{-1}$ were ratioed against those for standard, degassed, dried samples of Fisher Carbon Black. All the polymer samples were dried under vacuum at a minimum temperature of 50C. The plotted spectra, reproduced in Figures 5 through 20 , have been digitally smoothed using the standard software supplied as the Bruker ATS packages: smoothing does not have a significant influence upon the spectral appearance, or frequency maxima, of the major diagnostic peaks. Peak spectral frequencies are encoded and reproduced with the plots of spectra.

Figure 5
Sample KP-A
poly(p-Methoxystyrene)

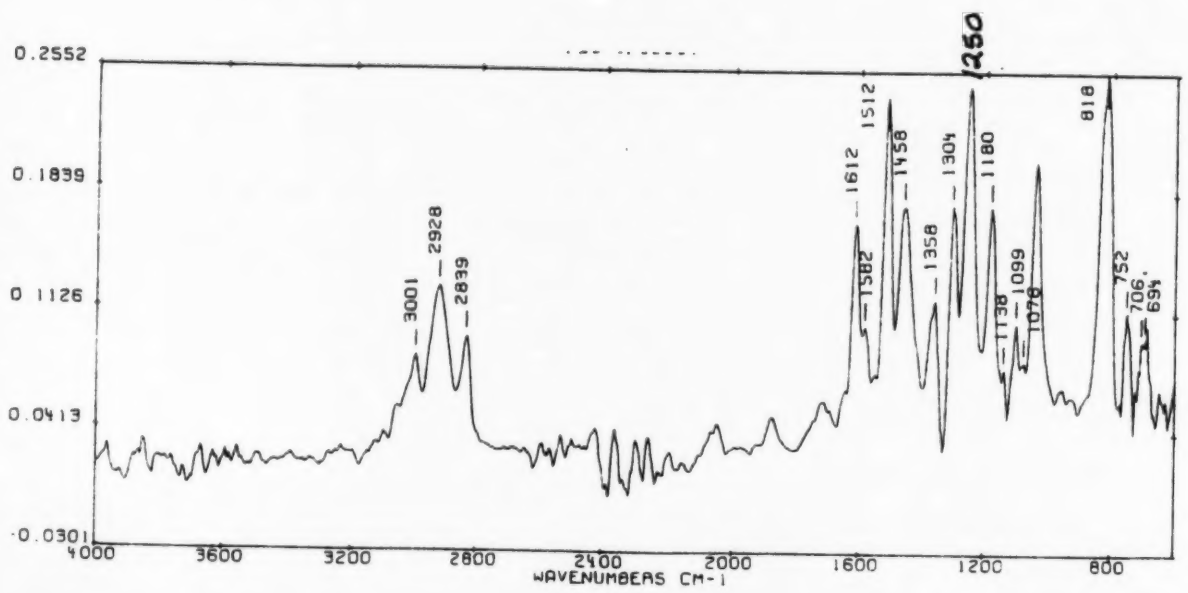


Figure 6

Sample KP-1

poly(p-Hydroxystyrene), poly(p-Vinylphenol

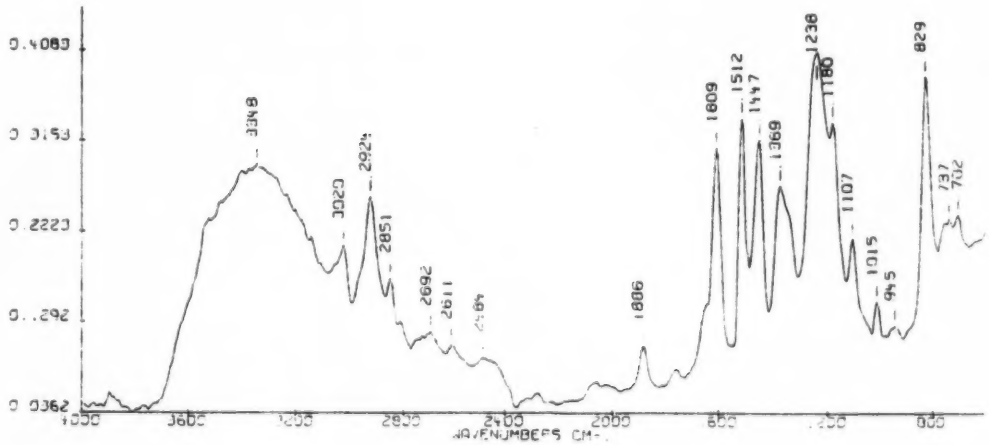


Figure 7
Sample KP-4
poly(Vinylbenzaldehyde)

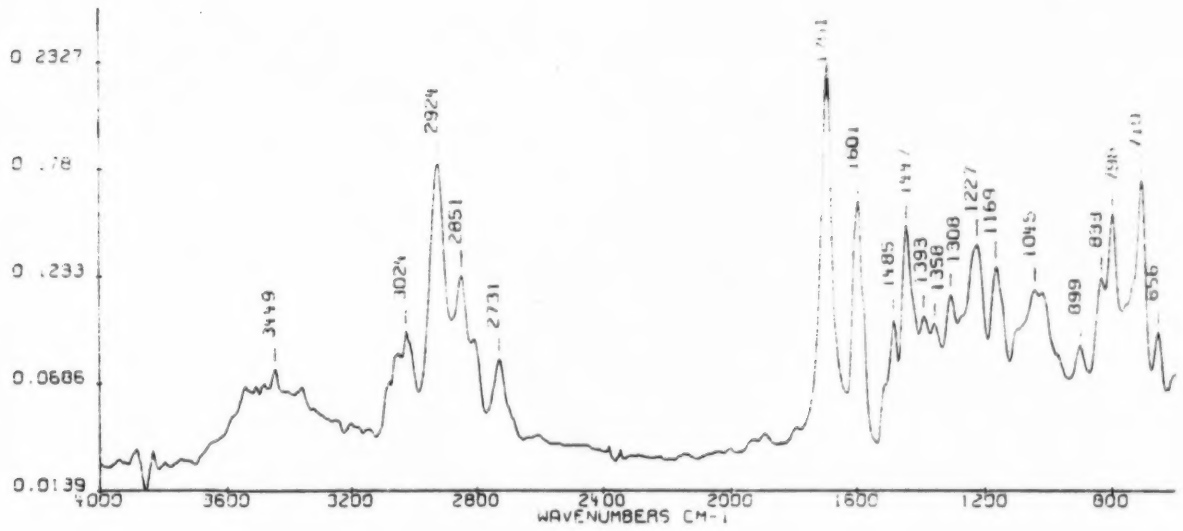


Figure 8
Sample KP-5
poly(Vinylbenzoic acid)

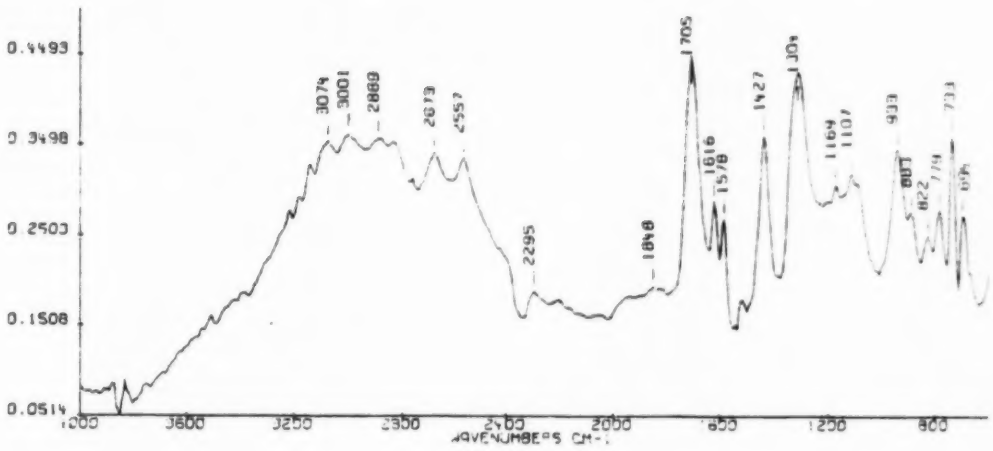


Figure 9

Sample KP-6

poly(p-Vinylphenyl acetate)

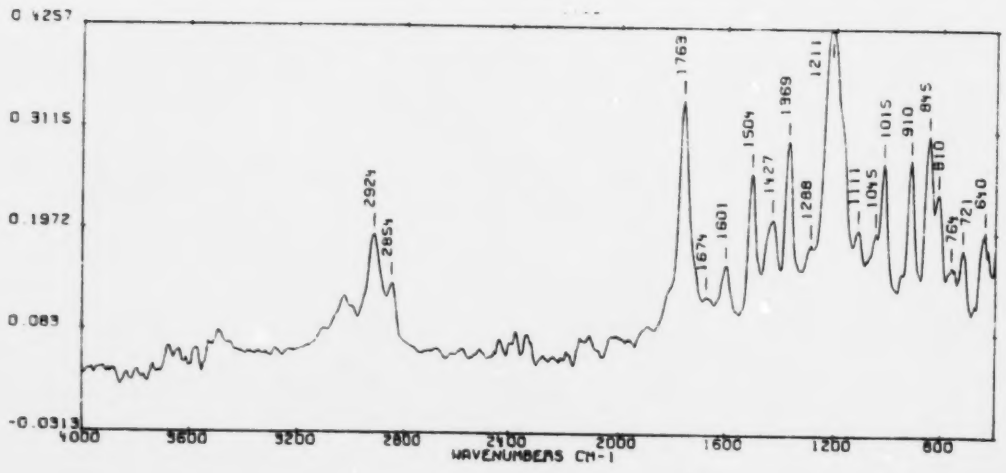


Figure 10
Sample KP-21
Sodium salt of poly(Vinylbenzoic acid)

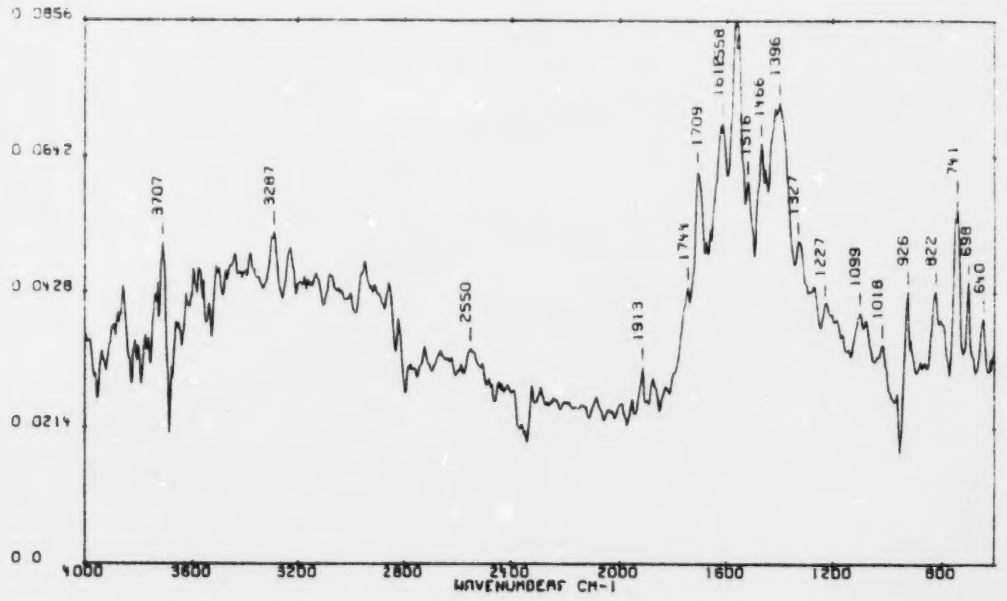


Figure 11
Sample KP-7
poly(Vinylacetophenone)

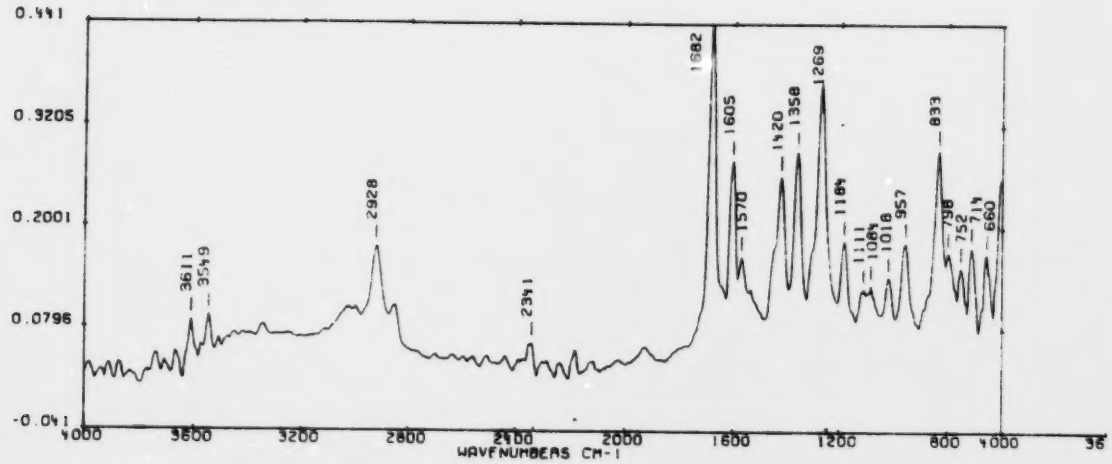


Figure 12

Sample KP-8

poly(3-Acetyl-4-methoxystyrene) + poly(Vinylphenyl acetate)

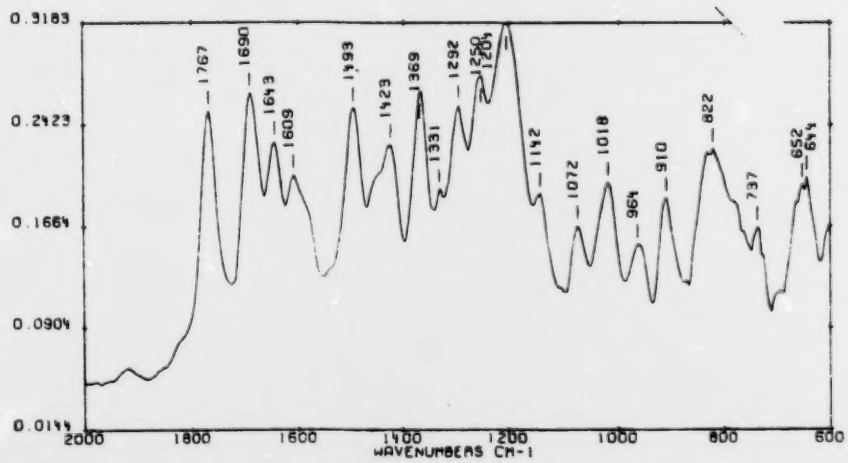


Figure 13
Sample KP-26
poly(Vinylacetophenonoxime)

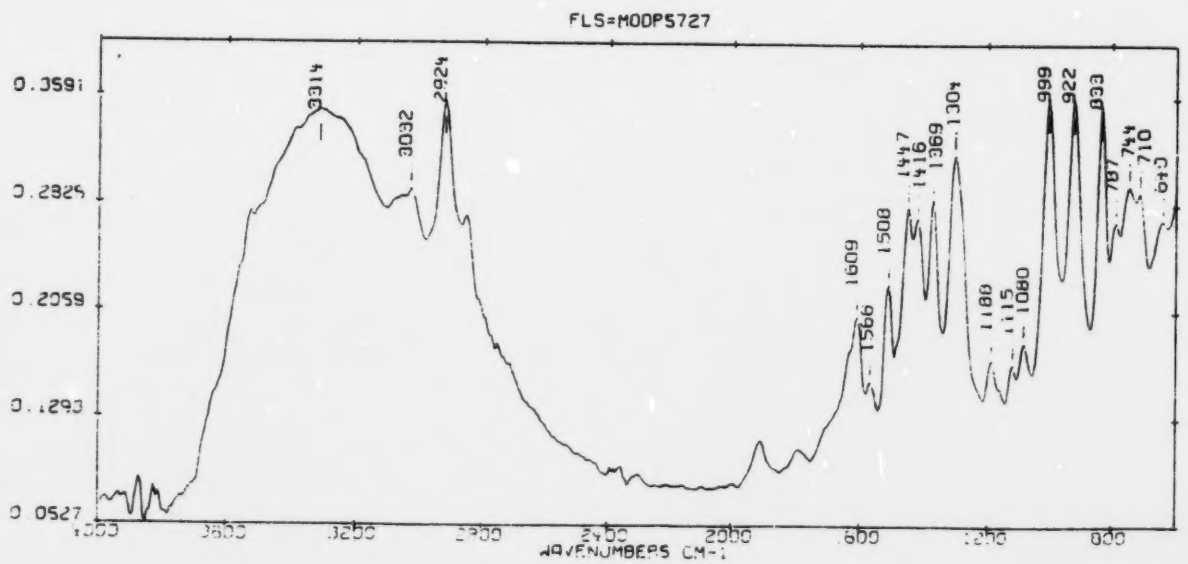


Figure 14
Sample KP-29
poly(3-Acetyl-4-hydroxystyrene)

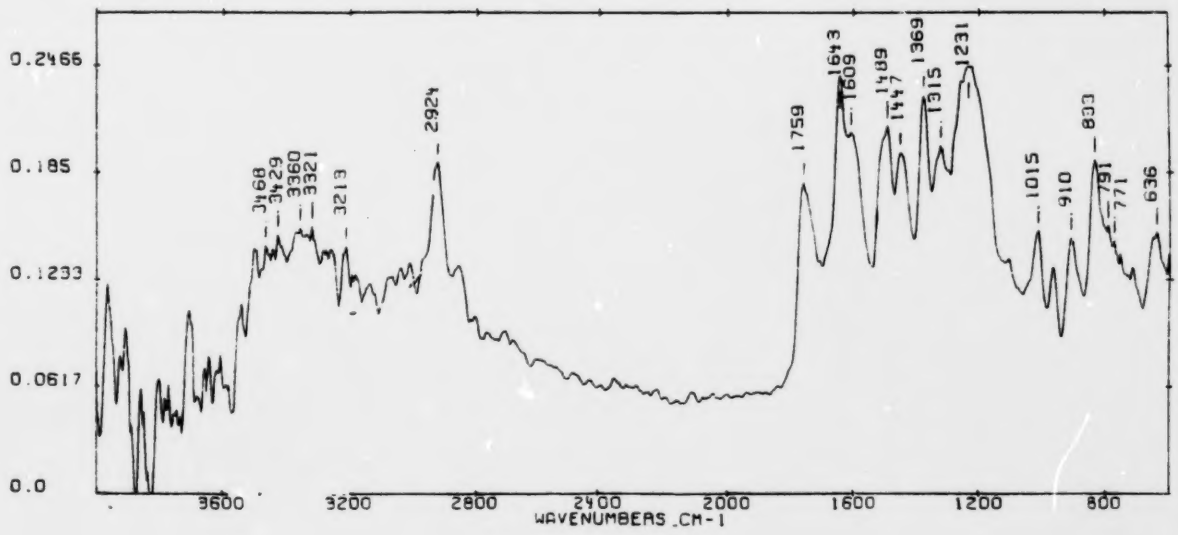


Figure 15
sample KP-31
poly(Vinylbenzophenone)

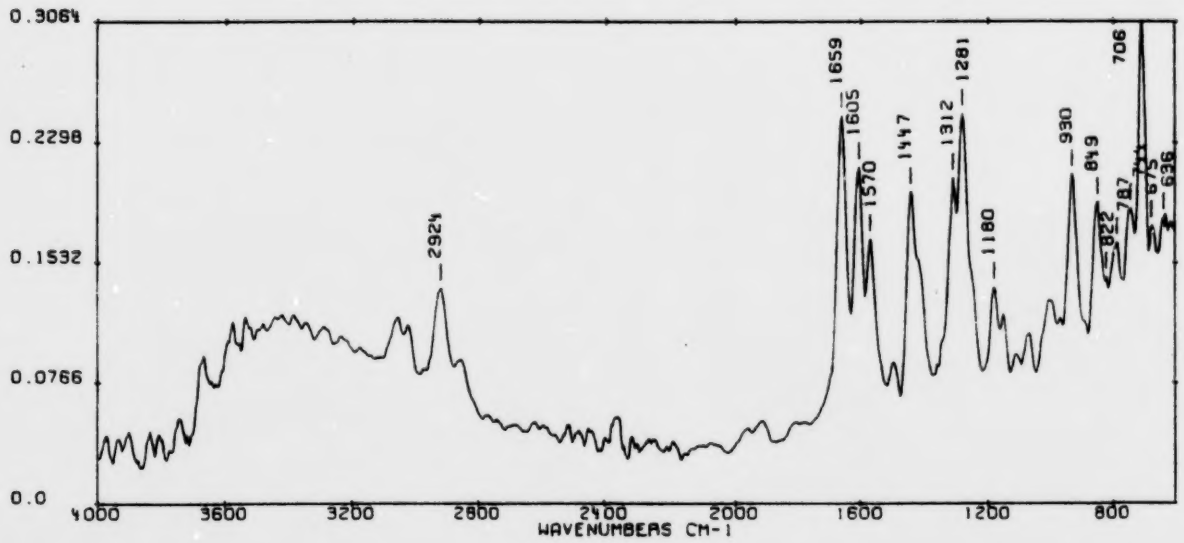


Figure 16
Sample KP-27
bis(poly(Vinylbenzyl) ether

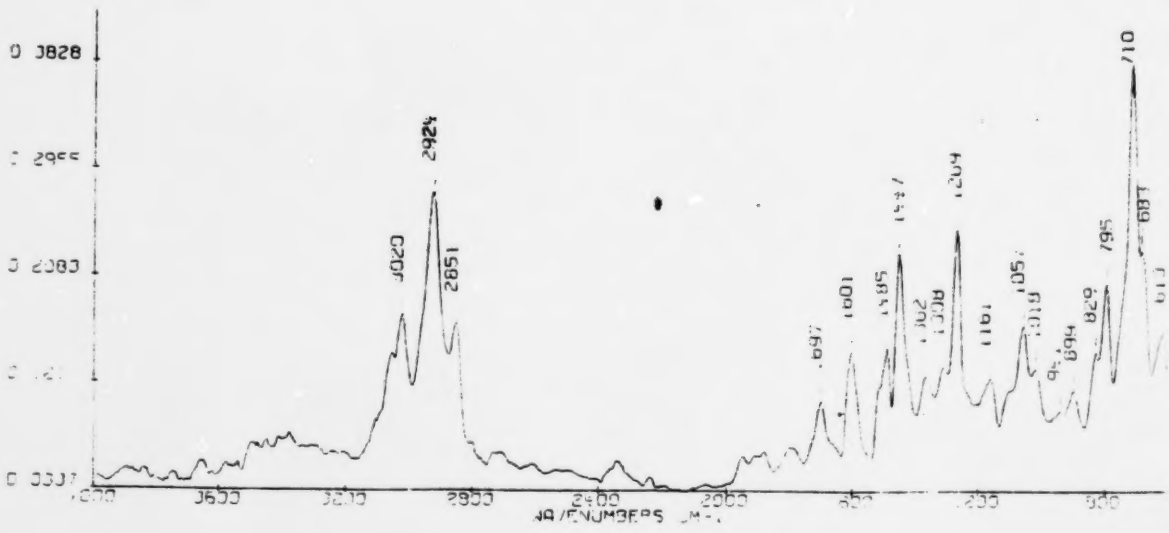


Figure 17
poly(Vinylbenzyl chloride)

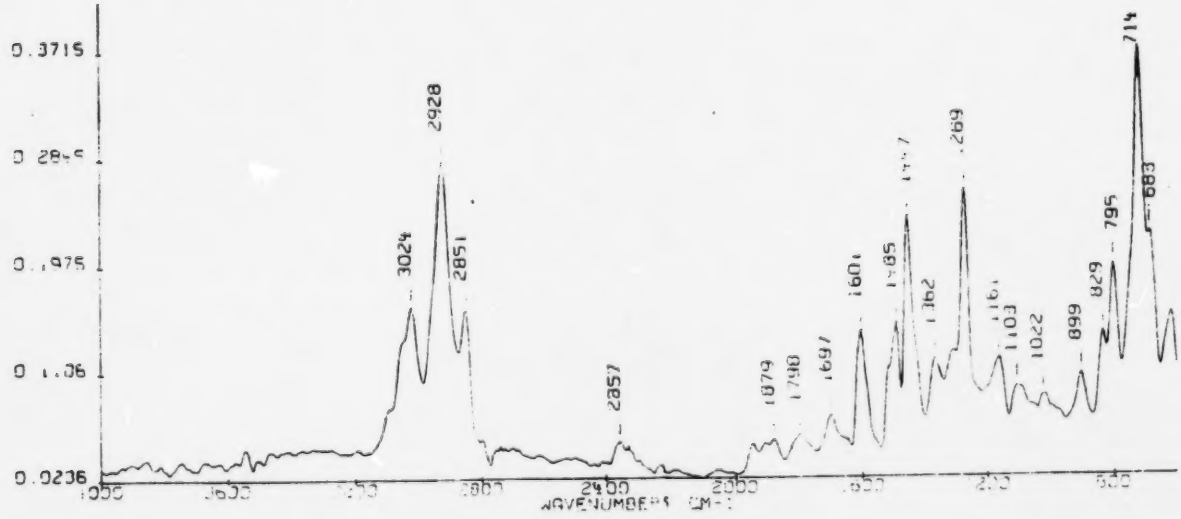
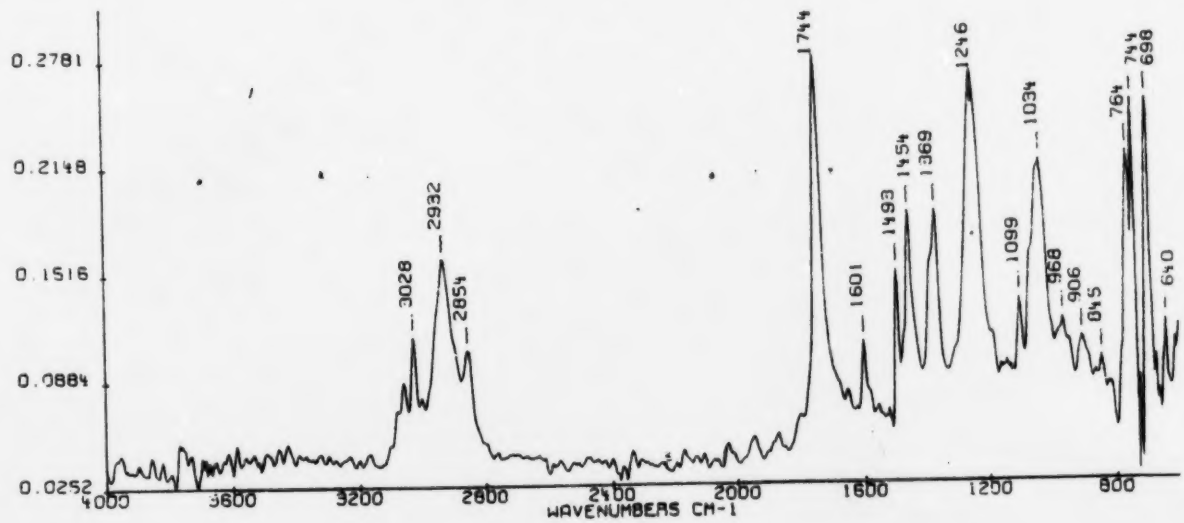


Figure 18
Sample LL-1
Allyl acetate/styrene copolymer

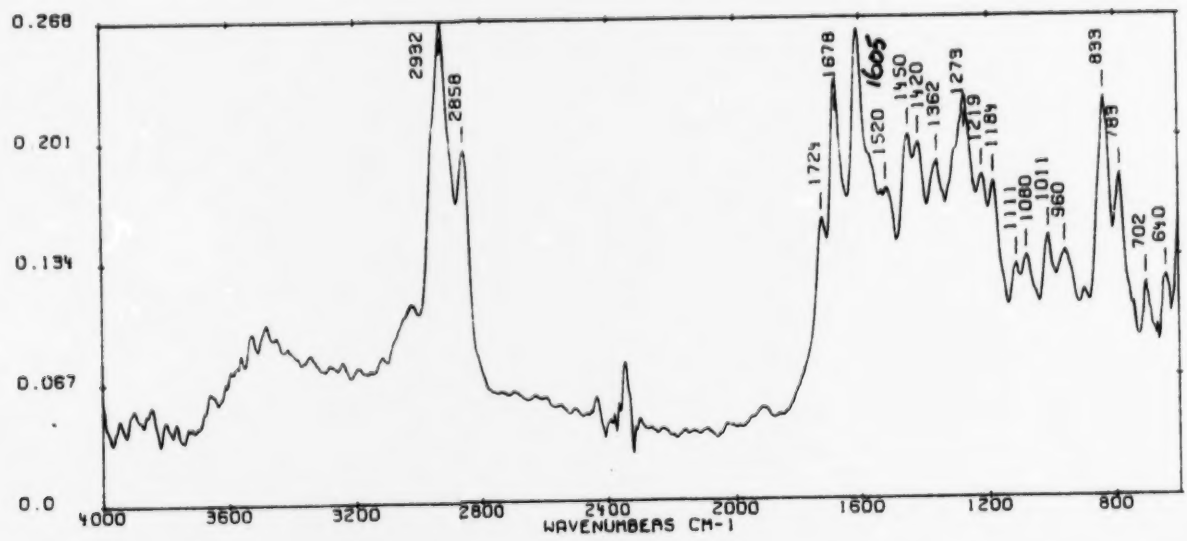


20

Figure 19

Sample KP-11

poly(Vinylphenylacetonylacetone)

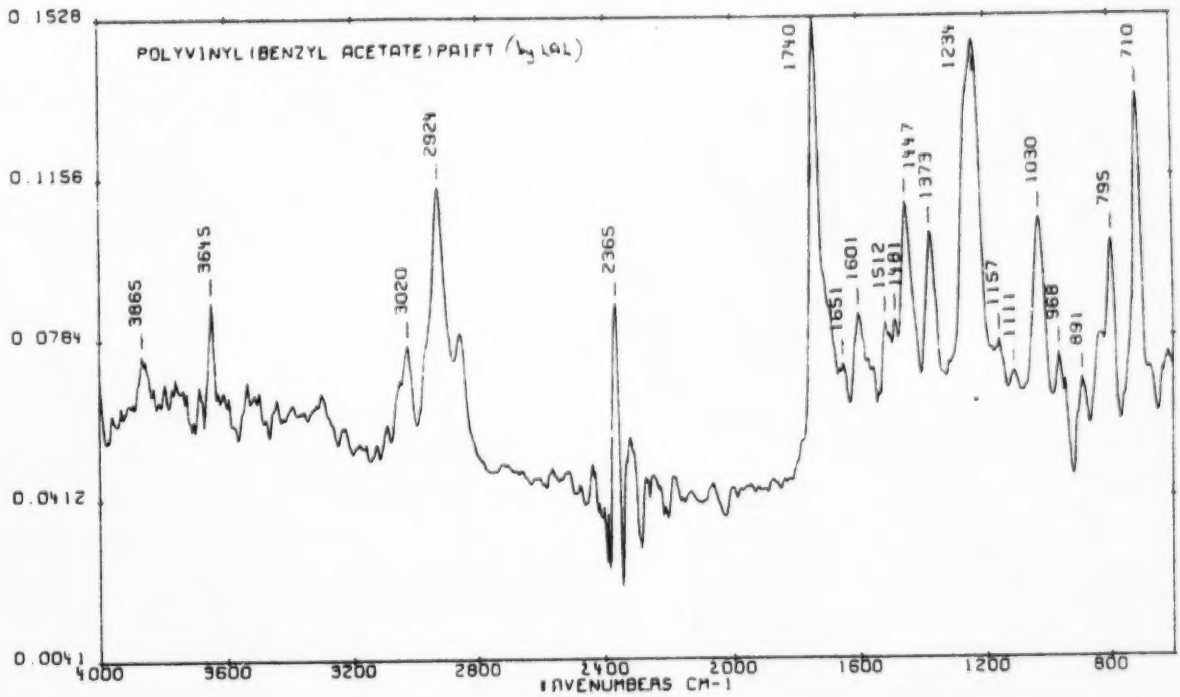


21

Figure 20

Sample KP-28

poly(Vinylbenzyl acetate)



KEY FEATURES AND COMPARISONS OF SPECTRA OF POLYMERS

Figure 5, Sample KP-A, poly(p-Methoxystyrene)
Ring vibrations at 1612, 1512 cm^{-1}
C-O Stretch of aromatic ether at 1250 $cm.^{-1}$
C-O Stretch of aliphatic ether at 1076 $cm.^{-1}$
Out-of-plane C-H deformation (2 adjacent H) for p-substituted ring at 818 $cm.^{-1}$

Figure 6, Sample KP-1, poly(p-vinylphenol)
Ring vibrations at 1609, 1512 $cm.^{-1}$
C-O Stretch of phenol at 1238 $cm.^{-1}$
out-of-plane C-H deformation: 829 $cm.^{-1}$
O-H Stretch, broad band with maximum at 3348 $cm.^{-1}$

Figure 7, Sample KP-4, poly(Vinyl benzaldehyde
Ring vibration at 1601 $cm.^{-1}$
Carbonyl stretch at 1701 $cm.^{-1}$
Aldehyde C-H stretch at 2731 $cm.^{-1}$
Out-of-plane C-H deformations at 833, 798, 710 $cm.^{-1}$

Figure 8, Sample KP-5, poly(Vinyl benzoic acid)
Ring vibrations at 1616, 1578 $cm.^{-1}$
Carbonyl stretch of carboxyl group at 1705 $cm.^{-1}$
Coupled C-O stretch and O-H deformation at 1304 $cm.^{-1}$
O-H Stretch, broad band from 3200-2550 $cm.^{-1}$

Figure 9, Sample KP-6, poly(p-Vinylphenyl acetate)
Ring vibrations at 1601, 1504 cm.$^{-1}$
Carbonyl stretch at 1763 cm.$^{-1}$
C-O Stretch at 1211 cm.$^{-1}$
Out-of-plane C-H deformation at 845,810 cm.$^{-1}$
Note absence of O-H stretch absorption, indicating quantitative acetylation (compare Figure 6).

Figure 10, Sample KP-6, sodium poly(Vinylbenzoate)
Antisymmetric and symmetric C-O stretch of carboxylate group at 1558 and 1396 cm.$^{-1}$
Note disappearance of carbonyl stretch for carboxylic acid group (compare Figure 8).

Figure 11, Sample KP-7, poly(Vinylacetophenone)
Ring vibrations at 1605 cm.$^{-1}$
Carbonyl stretch at 1682 cm.$^{-1}$

Figure 12, Sample KP-8, mixture of poly-(3-acetyl-4-methoxystyrene) and poly(p-vinylphenyl acetate)

Carbonyl stretch of O-acetyl group at 1767 cm.$^{-1}$
Carbonyl stretch of C-acetyl group at 1690 cm.$^{-1}$
C-O stretch of acetate at 1204 cm.$^{-1}$
C-O aromatic ether at 1250 cm.$^{-1}$

Figure 13, Sample KP-11, poly(Vinylacetophenonoxime)
Ring vibrations at 1609, 1508 cm.$^{-1}$
O-H stretch of :N-O-H at 3314 cm.$^{-1}$
Note disappearance of Carbonyl absorption (compare Figure 11)

Figure 14, Sample KP-29, poly(3-Acetyl-4-hydroxystyrene)

Ring vibrations, 1609 and 1489 cm.$^{-1}$
Hydrogen-bonded carbonyl at 1643 cm.$^{-1}$
unrearranged acetate carbonyl at 1759 cm.$^{-1}$
Hydrogen-bonded hydroxy stretch, 3500-3200 cm.$^{-1}$
C-O stretch from phenol at 1231 cm.$^{-1}$

Figure 15, Sample KP-31, poly(Vinylbenzophenone)

Ring vibrations, 1605 and 1570 cm.$^{-1}$
Carbonyl stretch at 1659 cm.$^{-1}$
This material may contain a little benzoic acid as contaminant.

Figure 16, Sample KP-27, bis(poly(Vinylbenzyl) ether
aliphatic ether feature from C-O stretch at 1057 cm.$^{-1}$
(contrast Figure 17)

Figure 17, poly(Vinyibenzyl chloride)
supplied for reference to previous figure: note absence of ether feature

Figure 18, Sample LL-1, allyl acetate/styrene copolymer
Weak ring vibration, 1601 cm.$^{-1}$
Aliphatic acetate carbonyl stretch at 1744 cm.$^{-1}$
C-O stretch from aliphatic acetate at 1246 cm.$^{-1}$
Note absence of any hydroxy absorption in 3500 cm.$^{-1}$ region (indicative of quantitative acetylation)

Figure 19, Sample KP-11, poly(Vinylphenylacetonylacetone)

Ring vibration at 1605 cm.$^{-1}$; note high intensity
Carbonyl stretch peaks at 1678 and 1724 cm.$^{-1}$
Hydroxyl stretch feature around 3500 cm.$^{-1}$ arises from keto-enol tautomeric form.

Figure 20, Sample KP-28, poly(Vinylbenzyl acetate)

Ring vibrations at 1601, 1512 cm.$^{-1}$
Aliphatic acetate carbonyl at 1740 cm.$^{-1}$
C-O stretch from aliphatic acetate at 1234 cm.$^{-1}$
Sloping baseline from 4000-3200 cm.$^{-1}$ may indicate some hydrolysis to poly(vinylbenzyl alcohol).

QUANTITATIVE AND QUALITATIVE ANALYSES OF POLYMER MIXTURES BY PAIFT SPECTROSCOPY

QUANTITATIVE

To test for the possibilities of quantitative analyses of polymer composites by photoacoustic infrared spectroscopy, test mixtures of the polymer samples KP-A (poly(p-methoxystyrene) and KP-7 (polyvinylacetophenone) were prepared in a range of weight percentages covering the extremes of composition. The individual components of the mixtures were ground in a Wig-l-Bug for 2 min, mixed together thoroughly using a mortar and pestle, and reground in the Wig-l-Bug for 30 s. The samples of mixtures were dried under vacuum at 50 C and the dried samples were stored in sealed vials.

Inspection of the PAIFT spectra for the two polymers (Figures 5 and 11) shows that there are marked differences in signal intensity in the 1600-1700 $cm.^{-1}$ region, illustrated further by the partial spectra in Figure 21.

Since differences in particle size between the differing components of the mixtures result in differing photoacoustic signal responses (note that the background and maximum intensities differ for the full spectra of Figures 5 and 11 and the partial spectra of Figure 21, which were the parent samples of the series of mixed polymers), we corrected for such effects by taking peak-height ratios for the characteristic peaks from the ring vibration in the poly(methoxystyrene) at 1600 $cm.^{-1}$ and for the carbonyl peak of the polyvinylacetophenone at 1680 $cm.^{-1}$

The peak-height ratios are plotted against percentage composition in Figure 22, illustrating a good-quality linear correlation between the peak-intensity ratio and composition for these mixed polymers.

Figure 21

Partial PAIFT Spectra, poly(Vinylacetophenone) (PVAP) and poly(Methoxystyrene) (PVA)

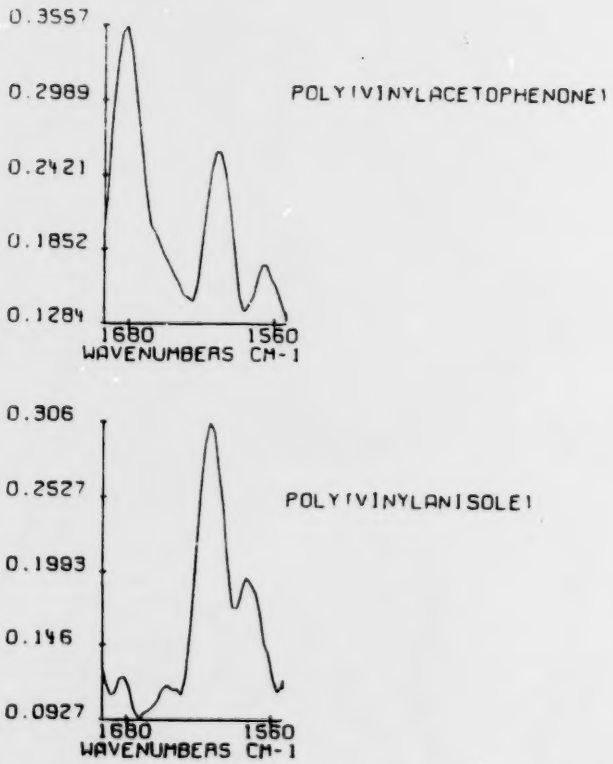
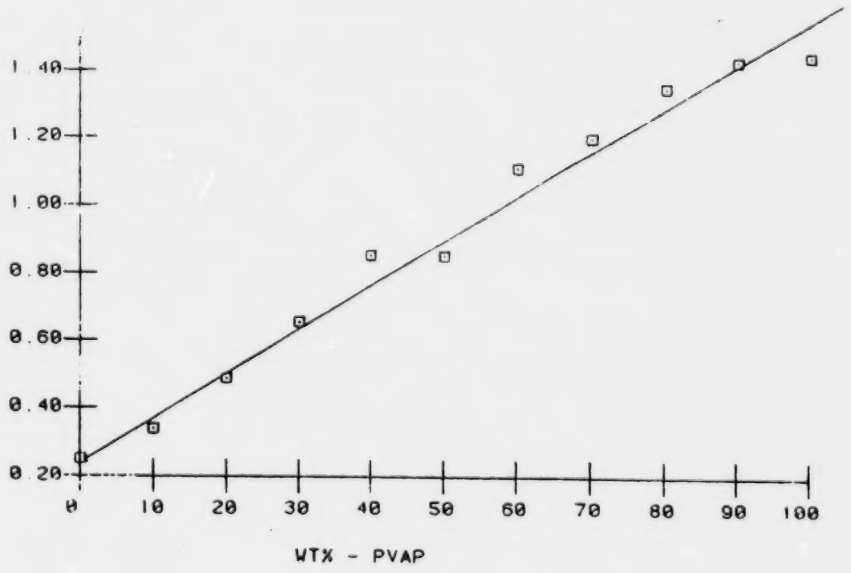


Figure 22
Peak height ratio vs. composition, PVAP-PVA mixtures



QUALITATIVE

Painter and his co-workers (R. W. Snyder, P. C. Painter, J. R. Havens, and J. L. Koenig, Applied Spectroscopy, 37, 497 (1983)) have made the revolutionary claim that alcoholic hydroxy groups are present in coals in a proportion of approximately 1/4 of the total hydroxyl. Their line of argument is based upon the detection of contributing peaks in the difference spectrum from acetylated coals of various ranks using the evidence from peaks in the second derivatives to identify contributing features. The intensities of these peaks are barely above noise perturbations.

We have tested the sensitivity of this method by examination of synthetic mixtures of poly(vinylphenyl acetate) and allyl acetate/styrene copolymer (compare Figures 9 and 18). The spectra for these measurements were encoded at 2 $cm.^{-1}$ intervals and the carbonyl maxima differ slightly from those in the earlier figures.
Figure 23 shows the spectra in the 1800-1600 $cm.^{-1}$ region for the two species. The partial spectra of 4:1 and 9:1 mixtures by weight of these acetylated polymers are reproduced in Figures 24 and 25, and the (inverted) second derivatives of the spectra are reproduced in Figures 26 and 27. It is evident that 20 and 10% proportions of alcoholic hydroxy groups are readily detectable in synthetic mixtures of acetylated species, so that if the proportion of alcoholic hydroxy suggested for coals by Painter and his co-workers were actually present, it should be readily visible as contributions to the second derivative peak structure. In other work in course of publication (B. M. Lynch and L. Lancaster, Proc. NATO Advanced Study Institute, "Applications of new Spectroscopic Techniques to Coal Science", Martinus Nijhoff, 1985), we have examined the PAIFT spectra of a wide range of acetylated bituminous and sub-bituminous coals, and have deen unable to confirm the results reported by Painter and co-workers. We suggest that the discrepancy results from the use of the KCl disk technique, and transmission spectroscopy, in their examination of samples.

Figure 23

1800-1600 cm.$^{-1}$ Absorptions in PAIFT spectra of allyl acetate/styrene copolymer (left) and poly(vinylphenyl acetate) (right)

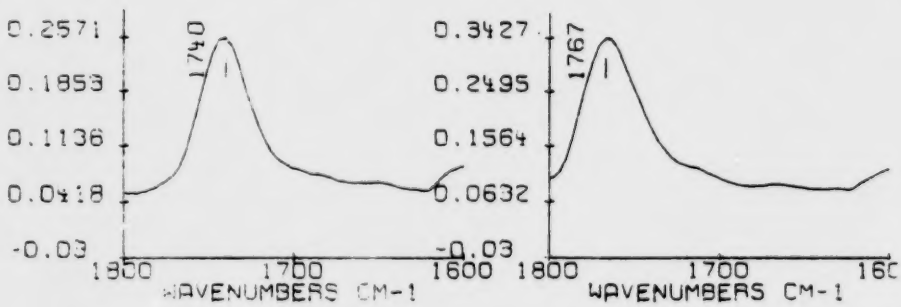


Figure 24

1800-1600 cm.$^{-1}$ Absorptions for 4:1 synthetic mixture of poly(vinylphenyl acetate) and allyl acetate/styrene copolymer

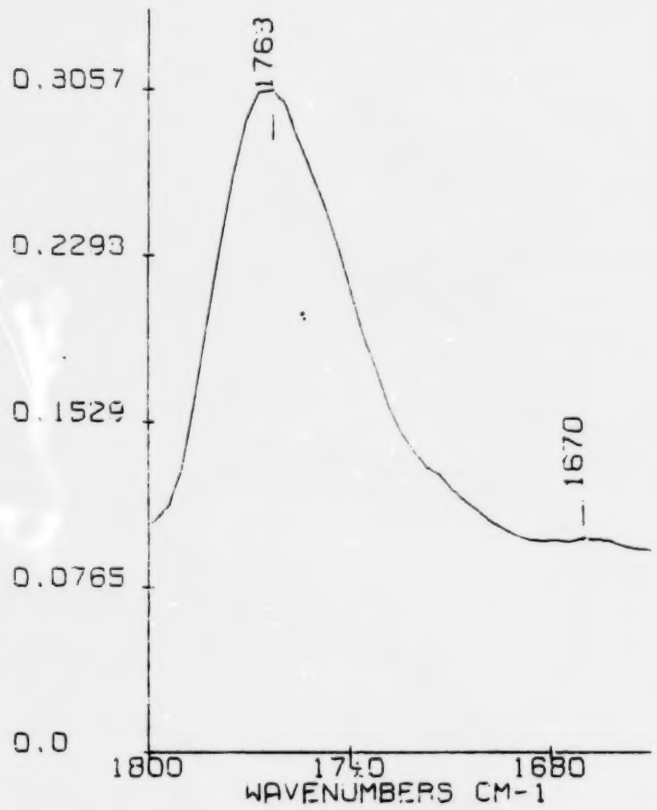


Figure 25

1800-1600 cm.$^{-1}$ Absorptions for 9:1 synthetic mixture of poly(vinylphenyl acetate) and allyl acetate/styrene copolymer

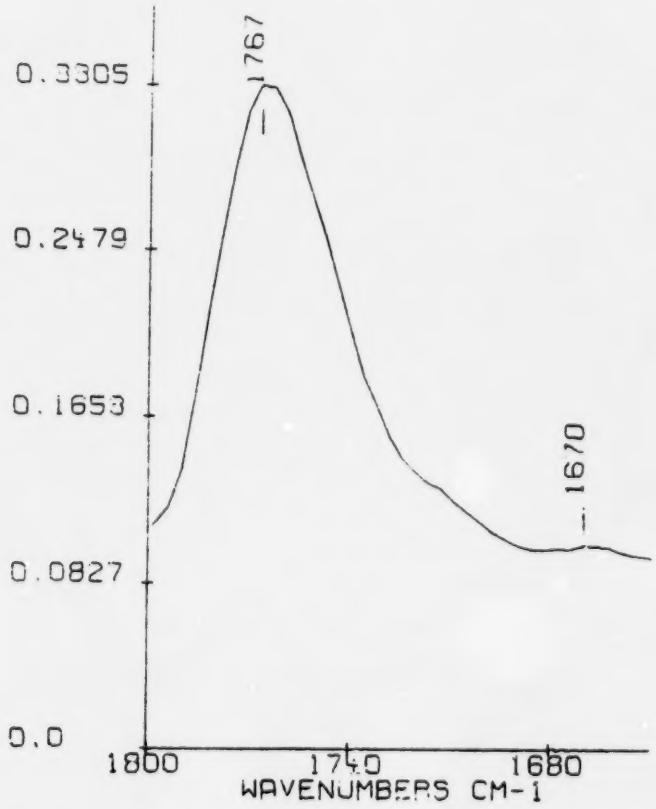


Figure 26

Inverted Second Derivative, 1800-1600 cm.$^{-1}$ region, for 4:1 synthetic mixture of poly(vinylphenyl acetate) and allyl acetate/styrene copolymer

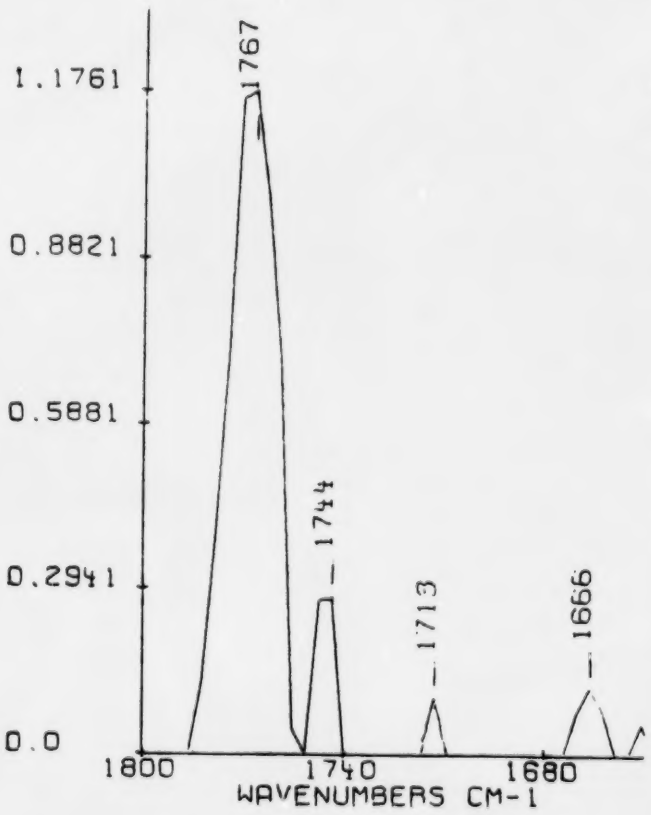
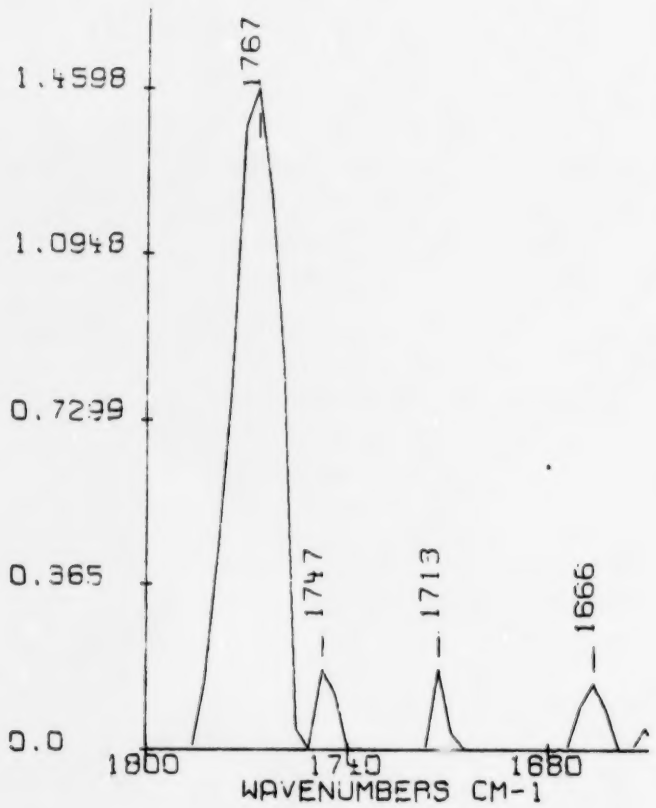


Figure 27
Inverted Second Derivative, 1800-1600 cm.$^{-1}$ region, for 9:1 synthetic mixture of poly(vinylphenyl acetate) and allyl acetate/styrene copolymer



1

EXPERIMENTAL PROCEDURES FOR SYNTHESES OF MODEL POLYMERS

Demethylation of poly(p-methoxystyrene) to poly(p-hydroxystyrene)

(KP-1)

Poly(p-methoxystyrene) (Aldrich chemical Company) (4.0 g) was heated under reflux with 48 % hydriodic acid (100 mL) for 24 h.
The precipitate obtained on cooling was washed with water and with sodium hydrogen sulfite, providing 3.0 g of demethylated material.

Hydrolysis/oxidation of poly(vinylbenzyl chloride) to poly(vinylbenzaldehyde)

(KP-4)

Poly(vinylbenzyl chloride) (Aldrich Chemical Company) (25 g) was stirred in methyl sulfoxide (150 mL) containing sodium hydrogen carbonate (9.5 g) at 155 degrees Celsius for 6 h, and the reaction mixture was allowed to cool and the precipitated material was collected by suction filtration. The solid was treated successively with methyl sulfoxide, hot water, 2:1 (v/v) dioxan/water, dioxan, dioxan, acetone, ethanol, and benzene, and dried under vacuum.
22.5 g of product was obtained.

2

Oxidation of poly(vinylbenzaldehyde) to poly(vinylbenzoic acid)

(KP-5)

Poly(vinylbenzaldehyde) (15 g) (sample KP-4) was added to a solution of potassium permanganate (100 g) and sodium hydroxide (30 g) in water (300 mL), and the reaction mixture was heated under reflux for 18 h. Filtration followed by decolorization with saturated aqueous sodium bisulfite, and acidification, precipitated the poly(vinylbenzoic acid), which was collected by filtration and dried at 110 degrees Celsius. The yield of dried product was 7.5 g.

Acetylation of poly(p-hydroxystyrene) to poly(p-acetoxystyrene) (poly-(p-vinylphenylacetate))

(KP-6)

Poly(p-hydroxystyrene) (1 g) (KP-1) was stirred with acetic anhydride (20 mL) and pyridine (1 mL) for 18 h, and poured into ice-water (300 mL), allowed to stand for 4 h, filtered, washed with water, and dried at 100 degrees Celsius. Approximately 1 g. of product was obtained.
Analysis: C, 73.18; H, 5.86; O, 19.52 %. C10H10O2 requires C, 74.05; H, 6.21; O, 19.73 %.

3

Acetylation of polystyrene to poly(vinylacetophenone)

(KP-7)

Dried polystyrene (Aldrich Chemical Company) (25 g) was dissolved in carbon disulfide (500 mL) in a reflux assembly (flask and condenser) protected from moisture by a calcium chloride guard tube.

Anhydrous aluminum chloride (65 g) was added in small portions with stirring over 0.5 h. Acetyl chloride (30 mL) was added and the reaction mixture was heated under reflux for 6 h and allowed to stand at laboratory temperature for a further 18 h.

The solid material was separated by filtration and was treated with successive washings with a total of 3 L of cold aqueous 5 % hydrochloric acid, then washed exhaustively with water until a test for soluble chloride was negative.

the resulting product was dried at 110 degrees Celsius.

The yield of dried product was 35 g.

Analysis: C, 77.57; H, 6.87; O, 10.60 %. C10H10O requires C, 82.15; H, 6.89; O, 10.94 %.

4

Acetylation of poly(vinylnaphthalene)

(KP-14)

Poly(vinylnaphthalene) (1.0 g) (Aldrich Chemical Company) was acetylated using the general conditions employed for the synthesis of polymer KP-7. The yield of product was 1.2 g.

Copolymerization of p-methoxystyrene and styrene

(KP-15)

p-Methoxystyrene (18.26 g), styrene (15.0 g) and benzoyl peroxide (0.3 g) in toluene (250 mL) were heated under rfelux for 12 h. The mixture was concentrated by removal of toluene under reduced pressure and diluted with methanol (200 mL), yielding the solid copolymer (15.5 g) after collection by filtration and drying at 100 degrees Celsius.

Demethylation of p-methoxystyrene/styrene copolymer

(KP-16)

The copolymer (1.0 g) was demethylated by heating under reflux with hydriodic acid (30 mL), followed by dilution with water, thorough washing, collection by filtration, and drying in air.

5

Sodium poly(vinylbenzoate)

(KP-21)

A small amount of the poly(vinyl benzoic acid) (KP-5) was neutralized with aqueous sodium hydrogen carbonate, filtered, and the water was evaporated, and the residue dried overnight at 100 degrees Celsius.

Oxime of poly(vinylacetophenone)

(KP-26)

Poly(vinylacetophenone) (0.50 g) (KP-7) and hydroxylamine hydrochloride (0.50 g) in pyridine (5 mL) were heated under reflux for 3 h, diluted with water (50 mL), collected by filtration, washed thoroughly on the filter with water, and dried at 100 degrees Celsius.

Synthesis & Characterization of Polymer Model Compounds - Appendix

Poly(vinylbenzyl ether) from poly(vinylbenzyl chloride)

(KP-27)

Poly(vinylbenzyl chloride) (1.0 g) (Aldrich Chemical Company) and potassium hydroxide (2.0 g) were stirred at room temperature in methyl sulfoxide (10 mL) for 10 h. Water (2.0 mL) was added and a further portion of methyl sulfoxide (10 mL), and stirring was continued for a further 10 h.
The product was isolated by filtration after the reaction mixture was poured into water (200 mL) and was dried under vacuum at 50 degrees Celsius.

Poly(vinylbenzyl acetate) from poly(vinylbenzyl chloride)

(KP-28)

Poly(vinylbenzyl chloride) (1.0 g) and anhydrous potassium acetate (2.0 g) were stirred in methyl sulfoxide (20 mL) for 10 h. The product was collected by filtration after the reaction mixture was poured into water (200 mL), and was dried under vacuum at 50 degrees Celsius.

7

Poly(3-acetyl-4-hydroxystyrene) from Fries Rearrangement of poly(p-acetoxystyrene)

(KP-29)

Poly(p-acetoxystyrene) (3.0 g) (KP-6) and anhydrous aluminum chloride (2.0 g) were heated together at 150-170 degrees Celsius for 15 min. The molten reaction mixture was poured on to ice shavings (100 g) and concentrated hydrochloric acid (10 mL) was added and the resulting suspension was stirred for 3 h. the product was collected by suction filtration, washed with water, and dried at 100 degrees Celsius. Approximately 2.2 g of product was obtained.
Analysis: C, 74.79; H, 6.01; O, 16.49 %. C10H10O2 requires C, 74.05; H, 6.21; O, 19.73 %.

Benzoylation of polystyrene to poly(vinylbenzophenone)

(KP-31)

Polystyrene (5.3 g) was dissolved in carbon disulfide (200 mL) by stirring for 30 min. Anhydrous aluminum chloride (14 g) was added and stirring was continued for a further 30 min. To this mixture was added benzcyl chloride (8.5 mL). Heating at reflux was applied for 4 h and the reaction mixture was allowed to cool to laboratory temperature. The precipitated solid was collected by suction filtration and treated with cold 5 % hydrochloric acid (1 L) and washed with water until the washings were free of chloride, then successively with water, saturated sodium hydrogen carbonate, hot and cold water, and ethanol.
The product was then dried at 100 degrees. 10.2 G. of benzoylated species was obtained.